



General synthesis, structure, and optical properties of benzothiophene-fused benzoheteroles containing Group 15 and 16 elements



Mio Matsumura^a, Atsuya Muranaka^{b,c,*}, Rina Kurihara^d, Misae Kanai^c, Kengo Yoshida^c, Naoki Kakusawa^d, Daisuke Hashizume^e, Masanobu Uchiyama^{b,c,f}, Shuji Yasuike^{a,*}

^a School of Pharmaceutical Sciences, Aichi Gakuin University, 1-100 Kusumoto-cho, Chikusa-ku, Nagoya 464-8650, Japan

^b Elements Chemistry Laboratory, RIKEN, Wako 351-0198, Japan

^c Advanced Elements Chemistry Research Team, RIKEN, Center for Sustainable Resource Science (CSRS), Wako 351-0198, Japan

^d Faculty of Pharmaceutical Sciences, Hokuriku University, Ho-3 Kanagawa-machi, Kanazawa 920-1181, Japan

^e Materials Characterization Support Unit, RIKEN Center for Emergent Matter Science (CEMS), Wako 351-0198, Japan

^f Graduate School of Pharmaceutical Sciences, The University of Tokyo, Tokyo 113-0033, Japan

ARTICLE INFO

Article history:

Received 23 August 2016

Received in revised form 17 October 2016

Accepted 18 October 2016

Available online 19 October 2016

Keywords:

Benzothieno[3,2-*b*]benzoheterole

Tetracyclic heteroacene

Group 15 and 16 elements

Comprehensive synthesis

Molecular structure

DFT calculation

ABSTRACT

A series of benzothieno[3,2-*b*]benzoheteroles containing Group 15 (N, P, As, and Sb) and Group 16 (O, S, Se, and Te) elements were synthesized by a versatile method. X-ray analyses revealed that all the tetracyclic heteroacene skeletons were planar. A linear relationship was found between the excitation energies of Group 16-heteroacenes and their atomic radius, in contrast to Group 15-heteroacenes. Density functional theory calculations and electrochemical measurements were performed to understand the structure–optical property relationship.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Linearly fused heteroacenes are attracting increasing interest owing to their intriguing potential for application in organic semiconductors for organic field-effect transistors (OFETs).¹ Among them, benzothieno[3,2-*b*]benzothiophene and its derivatives (**I**) have been widely investigated, leading to the development of high-performance organic semiconductors.^{1c,e,2} In connection with these studies, the benzothiophene-fused benzoheteroles (**II**), such as nitrogen (M=N-R'),³ phosphorus (M=P-R'),^{3d,4} oxygen (M=O),⁵ and selenium (M=Se)^{1c,e,2c,6} derivatives, have been sporadically prepared to develop synthetic routes and investigate their fundamental, electrochemical, and electronic device properties (Fig. 1). However, to the best of our knowledge, comprehensive synthesis of these heteroacenes has never been carried out. We have been

extensively working on the development of novel synthetic methodologies for a library of heterocycles containing Group 15 (N, P, As, and Sb) and Group 16 (O, S, Se, and Te) elements, and have already reported the synthesis and physical properties of 1-benzo[*b*]heteroles containing a series of Group 15 and 16 elements.⁷ In these articles, replacement of the Group 16 heteroatom leads to a considerable spectral shift, depending on the size of the heteroatom. Here, we report a convergent synthesis of benzothiophene-fused tetracyclic heteroacenes⁸ and a detailed comparison of the molecular structures and optical properties of the obtained heteroacenes. For the Group 15-heteroacenes, 10-phenyl derivatives were targeted because of the stability and handling ability.

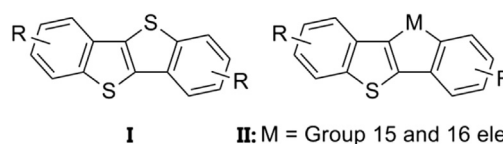


Fig. 1. Benzothiophene-fused tetracyclic heteroacenes.

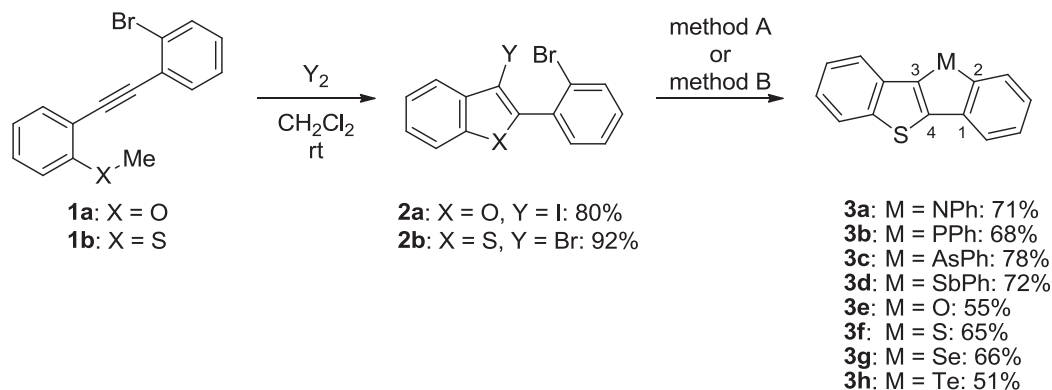
* Corresponding authors. Fax: +81 48 467 2879 (A.M.); fax: +81 52 757 6799 (S.Y.); e-mail addresses: atsuya-muranaka@riken.jp (A. Muranaka), s-yasuik@dpc.agu.ac.jp (S. Yasuike).

2. Results and discussion

The established convergent synthetic routes to benzothiophene-fused benzoheteroles **3** are shown in Scheme 1. The key precursors **2a** and **2b** were synthesized by I₂- and Br₂-mediated electrophilic cyclization of simple diphenyl acetylenes **1a** and **1b**, respectively.⁹ When **1a** was reacted with Br₂, the desired 2-halophenyl benzofuran derivative was not obtained but the triple bond underwent bromine addition to form a 1,2-dibromoalkene. Compound **2** was treated with *n*- or *t*-BuLi in anhydrous diethyl ether under an argon atmosphere, followed by trapping of the

dilithio intermediate with an electrophilic reagent, which resulted in ring closure to afford a range of the desired benzothiophene-fused benzoheteroles (**3b–h**) in moderate yields. Indole derivative **3a** was synthesized by the reaction of **2b** and aniline in the presence of Pd₂(dba)₃ and tri-*tert*-butylphosphonium tetrafluoroborate at 125 °C.¹⁰

We successfully obtained single crystals of all the heteroacenes and then carried out X-ray analysis.^{2e,11} Selected bond lengths and angles are summarized in the Supplementary data, and the ORTEP drawings are provided in Fig. 2. Fig. 2 clearly shows that the tetracyclic skeletons are planar. As expected, with the increase in the



Scheme 1. Synthesis of benzothiophene-fused benzoheteroles. For **3a**; method A. aniline (0.5 mmol), **2b** (0.55 mmol), Pd₂(dba)₃ (22 mol %), P(*t*-Bu)₃HBF₄ (22 mol %), *t*-BuONa (1.7 mmol), and toluene (5 mL) at 125 °C. For **3b–d** and **f–h**; method B. **2b** (2.0 mmol), *n*-BuLi (2.4 equiv), Group 15 or 16 reagent (4 mmol), and diethyl ether (40 mL), at –20 °C to rt. For **3e**; method B. **2a** (2.0 mmol), *t*-BuLi (4 equiv), (PhSO₂)₂S (4 mmol), and diethyl ether (30 mL), at –78 °C to rt.

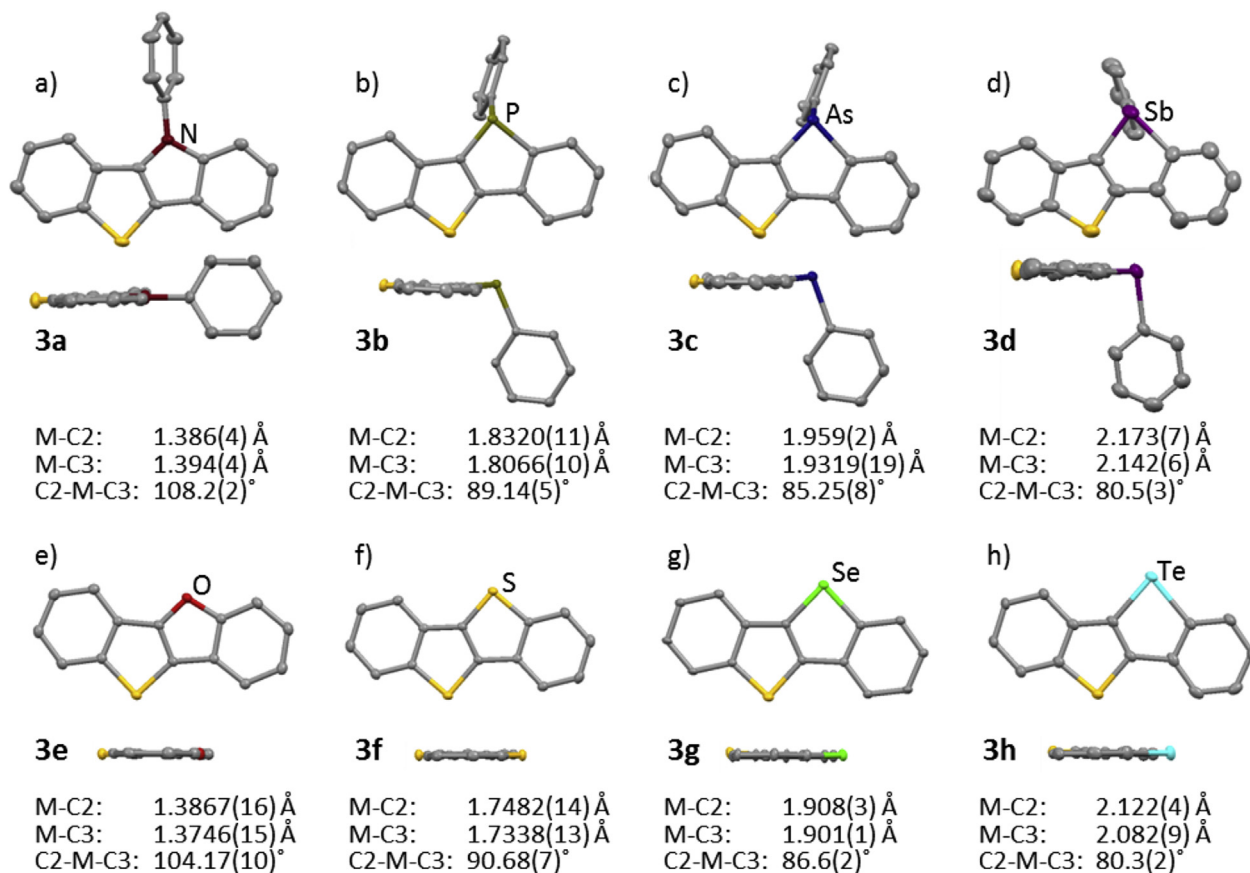


Fig. 2. Top views (top) and side views (bottom) of **3** in the solid state (50% probability level); the disordered atoms and hydrogen atoms are omitted for clarity. One of two geometries in the unit cell was drawn for **3d**.

Download English Version:

<https://daneshyari.com/en/article/5213338>

Download Persian Version:

<https://daneshyari.com/article/5213338>

[Daneshyari.com](https://daneshyari.com)